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(54) Title: SOLID PHASE EXTRACTION MEMBRANE

(57) Abstract

A wet-laid, porous solid phase extraction sheet material that contains both active particles and binder and that possesses excellent wet strength is described. The binder is present in a relatively small amount while the particles are present in a relatively large amount. The sheet material is sufficiently strong and flexible so as to be pleatable so that, for example, it can be used in a cartridge device.

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## SOLID PHASE EXTRACTION MEMBRANE

The invention was made with Government support under Subcontract 5 203690-A-F1, with Battelle Memorial Institute, Pacific Northwest Laboratories, based on a Contract DE-AC06-76RLO-1830 awarded by the United States Department of Energy. The United States Government has certain rights in the invention.

### 10 BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to a solid phase extraction sheet material that includes a porous matrix prepared by a wet-laid method, active particulate entrapped therein, and a binder. The sheet material exhibits improved properties 15 in comparison to similar sheet materials that do not include a binder.

#### 2. Background Information

Fibrous pulps can be converted to sheet materials by classic paper making methods generally known in the art as "wet-laid" or "handsheet" methods. In addition to the preparation of paper from a cellulose pulp, the preparation of sheet 20 materials useful as substrates for physical filtration processes and paper chromatography is also known.

Addition of particles to such fibrous pulps is also known. In U.S. Patent Nos. 5,300,192 and 5,352,480, wet-laid sheet materials that contain organic or inorganic particles capable of binding to an added binder compound (through 25 covalent or hydrogen bonding) are described.

Synthetic papers prepared from poly(*m*- or *p*-phenylene iso- or terephthalamide) fibers, widely known as aramid fibers, are known. Such aramid papers are commonly processes into dense, non-porous, stiff substrates such as substrates for circuit boards. See, e.g., U.S. Patent No. 4,729,921.

30 Aramid papers that include fillers have been described in, for example, U.S. Patent No. 4,548,678. Fillers are often used to alter the physical properties

or performance of the aramid paper. Commonly, filler-containing papers also are dense and non-porous.

A high porosity aramid paper that includes pulp from both fresh and previously dried (i.e., used or recycled) fibers but that does not contain particles or binder is described in U.S. Patent No. 5,026,456. Another porous aramid paper that does not contain particles or binder, but which is useful in physical filtration processes, is described in U.S. Patent No. 4,524,103.

A wet-laid aramid sheet material that contains reactive or sorptive particles is described in PCT Patent Document WO 95/17247. This sheet material is prepared in the absence of any binder and, accordingly, exhibits limited physical strength and tends to shrink when wet.

Not yet described in the art is a wet-laid aramid sheet material that contains reactive or sorptive particles and that possesses high wet strength and resistance to shrinkage.

15

## SUMMARY OF THE INVENTION

Briefly, the present invention provides a solid phase extraction sheet (i.e., a sheet that can remove one or more chemical species that are dissolved or entrained in a fluid) that includes a porous polymeric pulp, comprising a plurality of fibers, that mechanically entraps active particles and a polymeric hydrocarbon binder, the weight ratio of particles to binder being at least 13:1 and the ratio of average uncalendered sheet thickness to effective average particle diameter being at least 125:1.

Solid phase extraction (SPE) sheets can be used in place of particle-packed columns to remove solutes from fluids. Accordingly, the inclusion of large amounts of active particles in such sheets is desirable. In the SPE sheet of the present invention, particles are present in such an amount that the weight ratio of particles to binder is at least 13:1, preferably at least 14:1, and more preferably at least 15:1. A preferred amount of binder is about 5% (by weight). When this amount of binder is used, the amount of particles is about 65% (by wt.), preferably about 70% (by wt.), and more preferably about 75% (by wt.).

- In addition to the above-described ratio of particles to binder, the ratio of average uncalendered sheet thickness to effective average particle diameter in the SPE sheet of the present invention is at least 125:1, preferably at least 175:1, more preferably at least 200:1. Keeping both sheet thickness and particle diameter small
- 5 is desirable to keep extraction efficiency as high as possible. Nevertheless, if very small particles are used, the pressure drop across the SPE sheet becomes unreasonably high. Therefore, the average uncalendered sheet thickness is at least 125 times larger, preferably at least 175 times larger, more preferably 200 times larger, than the effective average particle diameter.
- 10 The SPE sheet of the present invention can be used in severe conditions where currently available SPE sheets, e.g., fibrillated polytetrafluoroethylene (PTFE) sheets, tend to degrade. An example of such severe conditions is in the highly caustic (i.e., pH of about 14), radioactive isotope-laden waste from some nuclear facilities. The radiation emitted by the radioactive isotopes of such waste
- 15 degrades PTFE SPE sheets.

As used herein, "active" means possessing ion exchange (i.e., reactive) or sorptive properties.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

20 The SPE sheet of the present invention comprises polymeric pulp, binder, and active particles. The use of binder allows particle loading levels and provides SPE sheets with good wet strength and resistance to shrinkage.

Generally, the fibers that make up the porous polymeric pulp of the SPE sheet of the present invention can be any pulpable fiber (i.e., any fiber that can be

25 made into a porous pulp). Preferred fibers are those that are stable to radiation and/or to a variety of pHs, especially very high pHs (e.g., pH = 14) and very low pHs (e.g., pH = 1). Examples include polyamide fibers and those polyolefin fibers that can be formed into a pulp including, but not limited to, polyethylene and polypropylene. Particularly preferred fibers are aromatic polyamide and aramid fibers because of their stability to both radiation and highly caustic fluids.

30 Examples of useful aromatic polyamide fibers are those fibers of the nylon family.

Examples of useful aramid fibers are those fibers sold under the trade name Kevlar™ (DuPont; Wilmington, DE). Pulps of such fibers are commercially available in various grades based on the length of the fibers that make up the pulp. Regardless of the type of fiber(s) chosen to make up the pulp, the relative amount of fiber in the resulting SPE sheet (when dried) ranges from about 12.5% to about 30% (by wt.), preferably from about 15% to 25% (by wt.).

Useful binders in the SPE sheet of the present invention are those materials that are stable over a range of pHs (especially high pHs) and that exhibit little or no interaction (i.e., chemical reaction) with either the fibers of the pulp or the particles entrapped therein. Polymeric hydrocarbon materials, originally in the form of latexes, have been found to be especially useful. Common examples of useful binders include, but are not limited to, natural rubbers, neoprene, styrene-butadiene copolymer, acrylate resins, and polyvinyl acetate. Preferred binders include neoprene and styrene-butadiene copolymer. Regardless of the type of binder used, the relative amount of binder in the resulting SPE sheet (when dried) is about 3% to about 7%, preferably about 5%. The preferred amount has been found to provide sheets with nearly the same physical integrity as sheets that include about 7% binder while allowing for as great a particle loading as possible.

Particles that can be incorporated in the SPE sheet of the present invention include those that, by ion exchange, chelation, covalent bond formation, size exclusion, or sorption mechanisms, bind and remove molecules and/or ions from fluids in which they are dissolved or entrained. Particles that undergo chemical reactions including oxidation and/or reduction are a particularly useful class. Representative examples include inorganic oxides such as silica, alumina, and zirconia, and derivatives thereof. Useful derivatives include polymeric coatings and moieties (such as C<sub>18</sub> alkyl chains, chelating ligands, and macrocyclic ligands) that are covalently bonded to the inorganic oxide particle. For an overview of such derivatized particles, see U.S. Patent Nos. 5,393,892, 5,334,326, 5,316,679, 5,273,660, 5,244,856, 5,190,661, 5,182,251, 5,179,213, 5,175,110, 5,173,470, 5,120,443, 5,084,430, 5,078,978, 5,071,819, 5,039,419, 4,996,277, 4,975,379, 4,959,153, 4,952,321, and 4,943,375.

Other useful particles include polymeric organic resins, such as styrene divinylbenzene and derivatives thereof. The particles can have ion exchange, chelation, or chiral separation properties. Hydrophobic zeolites such as those sold under the trade name Silicalite™ (UOP; Tarrytown, NY) are particularly useful in 5 an aramid fiber sheet for isolating volatile organic compounds since both components are stable at high temperatures. Carbon can be useful as a sorptive particulate in certain applications. Hydrophobic molecular sieves can be useful to sorb organic materials such as pollutants. Alumina coated with elemental gold is a useful reactive particulate in certain oxidation-reduction reactions, and to isolate 10 elemental mercury by amalgam formation with elemental gold.

Preferably, the effective average diameter of particles used in the SPE sheet of the present invention ranges from about 2 to 75  $\mu\text{m}$ , more preferably from about 9 to 18  $\mu\text{m}$ . The effective average diameter of the particles is at least 125 times smaller than the uncalendered thickness of the sheet, preferably at least 175<sup>15</sup> times smaller than the uncalendered thickness of the sheet, more preferably at least 200 times smaller than the uncalendered thickness of the sheet.

Because the capacity and efficiency of the SPE sheet depends on the amount of particles included therein, high particle loading is desirable. The relative amount of particles in a given SPE sheet of the present invention is 20 preferably at least about 65% (by wt.), more preferably at least about 70% (by wt.), and most preferably at least about 75% (by wt.). Additionally, the weight percentage of particles in the resulting SPE sheet is at least 13 times greater than the weight percentage of binder, preferably at least 14 times greater than the weight percentage of binder, more preferably at least 15 times greater than the 25 weight percentage of binder.

Regardless of the type or amount of the particles used in the SPE sheet of the present invention, they are mechanically entrapped or entangled in the polymeric fibers of the porous polymeric pulp. In other words, the particles are not covalently bonded to the fibers.

30 The SPE sheet of the present invention can also comprise one or more adjuvants. Useful adjuvants include those substances that act as process aids and

those substances that act to enhance the overall performance of the resulting SPE sheet. Examples of the former category include sodium aluminate and aluminum sulfate (commonly known as "alum"), which help to precipitate binder into the pulp, and dispersants or surfactants such as Tamoil<sup>TM</sup> 850 dispersant (Rohm &

5 Haas Co.; Philadelphia, PA). Examples of the latter category include crosslinking agents for the binder such as zinc oxide. When used, relative amounts of such adjuvants range from more than zero up to about 0.5% (by wt.), although their amounts are preferably kept as low as possible so as not to take away from the amount of particles that can be added.

10 To make the SPE sheet of the present invention, chopped fibers and a liquid, normally water, are added to a container and blended. The amount of shear used has not been found to affect the ultimate properties of the resulting SPE sheet, although the amount of shear introduced during blending is preferably high.

15 Thereafter, active particles, binder (in the form of a latex) and an excess of a pH adjusting agent such as alum, which acts to precipitate the binder, are added to the container. If an SPE sheet is to be made by hand-sheet methods known in the art, the order that these three ingredients are added does not significantly affect ultimate performance of the SPE sheet. However, addition of binder after addition of particles can result in an SPE sheet where binder is more likely to

20 adhere the particles to the fibers of the SPE sheet. Also, if an SPE sheet is to be made by a continuous method, the three ingredients must be added in the listed order. (The remainder of this discussion is based on the hand-sheet method, although those skilled in the art can readily recognize how to adapt that method to allow for a continuous process.)

25 After the particles, binder, and alum are added to the fiber-liquid slurry, this mixture is poured into a mold, the bottom of which is covered by a screen. Water is allowed to drain from the wet sheet through the screen. After sufficient water has drained from the sheet, the wet sheet is normally removed from the mold and dried by pressing, heating, or a combination of the two. Normally, pressures of 300 to 600 kPa and temperatures of 40° to 200°C, preferably 100° to 30 150°C, are used in these drying processes.

Once made, the SPE sheet of the present invention can be cut to the desired size and used as is. If desired, the SPE sheet can be calendered. Alternatively, where the polymeric pulp comprises long (i.e., about 4 mm) fibers, an uncalendered SPE sheet can be pleated so as to allow for inclusion in cartridge devices known in the art. To pleat the SPE sheet, it can be placed between two scrims and pleated by a variety of well known methods. The pleating can be traditional (in other words, parallel to the length of the cartridge device) or horizontal (in other words, perpendicular to the length of the cartridge device), as is described in U.S. Patent No. 4,842,739.

10        Regardless of form, the SPE sheet of the present invention can be used to remove solutes from fluids that pass through the SPE sheet. Preferably, the SPE sheet of the present invention can be used to remove radioactive isotopes from nuclear energy waste. Such waste can be highly acidic (e.g., pH = 1) or highly caustic (e.g., pH = 14) and radioactive.

15        Objects and advantages of this invention are further illustrated by the following examples. The particular materials and amounts thereof, as well as other conditions and details, recited in these examples should not be used to unduly limit this invention.

## 20        EXAMPLES

### Example 1

To an agitated slurry of 6 g Kevlar™ 6F543 dry aramid fiber pulp (DuPont) and 2000 mL water in a 4 liter blender was added 1.9 g of a 33% aqueous solution of sodium aluminate. After blending at a low speed setting for 25 30 seconds, 5 g (2 g dry weight) styrene-butadiene latex binder slurry (B.F. Goodrich Co.; Cleveland, OH) was added. Blending was continued for 15 seconds at a low speed before 12 g alum was added, with blending. At that point, binder precipitated onto the pulp. While blending of the slurry was continued, 32 g silica with an average diameter of 9 µm (Davison Chemicals Co.; Baltimore, 30 MD) in 500 mL water was added.

The mixture was poured into a sheet mold (Williams Apparatus Co.; Watertown, NY) with a  $930.3 \text{ cm}^2$  porous screen having pores of approximately 0.14 mm (i.e., 100 mesh) at the bottom to allow the water to drain. This gave a wet sheet, which was pressed in a pneumatic press (Mead Fluid Dynamics; 5 Chicago, IL) at 482 kPa for about five minutes to remove additional water. The sheet was dried on a hot plate at  $104^\circ\text{C}$  for 60 minutes, then at  $129^\circ\text{C}$  for another 10 minutes to give a dry sheet. The sheet had the following characteristics:

	average thickness	--	2.8 mm
	density	--	$0.33 \text{ g/cm}^3$
10	wt. % of particles in SPE sheet	--	73%
	basis weight	--	$936 \text{ g/m}^2$
	tensile strength	--	692 kPa.

(Density values throughout the Examples were calculated by dividing the listed basis weight by the listed average thickness.)

15 Tensile strength and elongation were measured according to ASTM method D882-91.

### Example 2

To an agitated slurry of 10 g Kevlar™ 1F306 dried aramid fiber pulp (Du Pont) and 2500 mL water in a 4 liter blender was added 1.9 g of a 33% aqueous 20 solution of sodium aluminate. After blending at a low speed setting for 30 seconds, 6.25 g (2.5 g dry weight) styrene-butadiene latex binder slurry was added. Blending was continued for 15 seconds at a low speed. To this mixture was added a slurry of 37.5 g silica particles (Davison Chemical) that had been previously coated with approximately 2 to 5 weight percent, based on the weight 25 of the silica particles, SuperLig™ 304 extractant (IBC Advanced Technologies, Inc.; Provo, UT) dispersed in 300 mL water. After 15 seconds of blending, 18 g alum was added with blending, and the binder precipitated onto the pulp and particulate.

A solid sheet was prepared from the slurry as described in Example 1. The wet sheet was pressed for 5 minutes at 413 kPa, then dried at 149°C for 30 minutes to give a dry sheet having the following characteristics:

	average thickness	--	2.8 mm
5	density	--	0.38 g/cm <sup>3</sup>
	wt. % particles in SPE sheet	--	74%
	basis weight	--	1061 g/m <sup>2</sup>
	tensile strength	--	1.98 MPa.

10

### Example 3

To an agitated slurry of 10 g Kevlar™ 1F306 dried aramid fiber pulp and 2500 mL water in a blender was added 1 g Tamol™ 850 dispersant. After blending at a low speed setting for 30 seconds, 113.3 g of a 33% (by wt.) aqueous slurry of particles of SuperLig™ 644 with an average particle size of 9.5 µm (IBC Advanced Technologies) was added with continued blending. Next, 6.25 g (2.5 g dry weight) styrene-butadiene latex binder slurry was added and blending was continued for 15 seconds at a low speed. To this mixture was added a solution of 12 g alum in 25 mL water, and blending was continued as the binder precipitated onto the pulp and particulate.

20

A handsheet was prepared from the mixture and pressed for 5 minutes at 620 kPa, then heated on a hot plate at 110°C for 45 minutes. The resultant dry sheet had the following characteristics:

	average thickness	--	2.4 mm
25	density	--	0.44 g/cm <sup>3</sup>
	wt. % particles in SPE sheet	--	69%
	basis weight	--	1060 g/m <sup>2</sup>
	tensile strength	--	2.4 MPa.

Samples of the dried sheet were then exposed to acidic, basic, and neutral solutions and tested for residual strength. In each case, a sample of the sheet was

soaked in the solution indicated for the amount of time shown, then removed and retested wet. The results are shown in Table 1.

Table 1

Sample	Tensile Strength (MPa)	% change from dry
Dry	2.4	--
Water <sup>1</sup>	2.8	+16
Acid <sup>2</sup>	2.3	-4
Base <sup>3</sup>	1.3	-45

5

<sup>1</sup> 21 days in deionized water.

<sup>2</sup> 2 days in 1 M aqueous HNO<sub>3</sub>.

<sup>3</sup> 21 days in 4 M aqueous NaOH.

10

A comparative sample (i.e., an SPE sheet made identically with the exception that no binder was added) was also made. This comparative sample had a (dry) tensile strength of 0.2 MPa. Its wet tensile strength could not be measured because it returned to a pulp when wetted.

15

#### Example 4

To an agitated slurry of 6 g Kevlar™ 6F543 dry aramid fiber pulp and 2000 mL water in a blender was added 1.9 g of a 33% aqueous solution of sodium aluminate. After blending at a low speed setting for 30 seconds, 4.36 g (1.75 g dry weight) styrene-butadiene latex binder slurry was added and blending was continued for 15 seconds at a low speed. To this mixture was added 12 g alum with blending, and the binder precipitated onto the pulp. Finally, 26.25 g zirconia particles having an average diameter of 11 µm (prepared as described in Example No. 5 of U.S. Patent No. 5,015,373) in 500 mL water was added with continued blending.

20

A sheet was prepared as described in Example 1. The sheet was pressed for 5 minutes under 413 kPa pressure, then heated for 30 minutes at 149°C and 10

minutes at 129°C on a hot plate. The resulting sheet had the following characteristics:

	average thickness	--	1.1 mm
5	density	--	0.81 g/cm <sup>3</sup>
	wt. % particles in SPE sheet	--	73%
	basis weight	--	895 g/m <sup>2</sup>
	tensile strength	--	5.9 MPa.

After 48 hours immersion in a 1 M HNO<sub>3</sub>, the sheet had a tensile strength of 2.8 MPa. This example demonstrates the excellent retention of strength shown by the 10 sheet of the present invention when a binder is used in its preparation.

#### Example 5

To an agitated slurry of 10 g Kevlar™ 1F306 dried aramid fiber pulp and 2000 mL water in a blender was added 1.9 g of a 33% aqueous solution of sodium aluminate. After blending at a low speed setting for 30 seconds, 8.37 g (3.35 g dry weight) styrene-butadiene latex binder slurry was added and blending was continued for 15 seconds at a low speed. To this mixture was added 18 g alum was added with blending, and the binder precipitated onto the pulp. Thereafter, a mixture of 53.6 g zirconia particles having an average diameter of 11 µm 15 (prepared as described in Example 4) in 500 mL water containing 1% (by wt.) potassium tripolyphosphate was added with continued blending.

20

A sheet was prepared as described in Example 1. The sheet was pressed for 5 minutes under 551 kPa pressure, then heated for 60 minutes at 104°C and 10 minutes at 129°C on a hot plate. The resulting sheet had the following 25 characteristics:

	average thickness	--	1.65 mm
30	density	--	1.0 g/cm <sup>3</sup>
	wt. % particles in SPE sheet	--	78%
	basis weight	--	1632 g/m <sup>2</sup>
	tensile strength	--	6.1 MPa.

After 18 days immersion in a 4 M NaOH, the sheet had a tensile strength of 2.3 MPa. This example demonstrates the excellent retention of strength shown by the sheet material of the present invention when a binder is used in its preparation.

5

### Example 6

To an agitated slurry of 6 g Kevlar™ 1F306 dried aramid fiber pulp and 2500 mL water in a blender was added 1.9 g of a 33% aqueous solution of sodium aluminate. After blending at a low speed setting for 30 seconds, 4.36 g (1.75 g dry weight) styrene-butadiene latex binder slurry was added and blending was 10 continued for 15 seconds at a low speed. To this mixture was added 12 g alum with blending, and the binder precipitated onto the pulp. The slurry was diluted with 200 mL isopropyl alcohol before 5 drops (approximately 0.5 mL) of a defoamer (Henkel Corp.; Ambler, PA) was added. Finally, 28 g zirconia particles having an average diameter of 11  $\mu\text{m}$  (prepared as in Example 4) and further 15 coated with approximately 2 to 5 weight percent, based on the weight of the zirconia particles, SuperLig™ 625 extractant (IBC Advanced Technologies) in 500 mL of a 90:10 solution of water-isopropanol containing 0.5 mL defoamer was 20 added with continued blending.

A sheet was prepared as described in Example 1. The sheet was pressed 25 for 5 minutes under 551 kPa pressure, then heated for 30 minutes at 109°C and 10 minutes at 149°C on a hot plate. The resulting sheet had the following characteristics:

	average thickness	--	1.26 mm
	density	--	0.80 g/cm <sup>3</sup>
25	wt. % particles in SPE sheet	--	69%
	basis weight	--	1012 g/m <sup>2</sup>

### Example 7

An agitated slurry of 9.9 g Kevlar™ 6F543 dry aramid fiber pulp and 3500 mL water in a blender was added 1.9 g of a 33% aqueous solution of sodium aluminate was stirred for 30 seconds. To this mixture was added 7.34 g (3.3 g dry weight) of a 45 weight percent aqueous styrene-butadiene latex binder slurry (DuPont), and the mixture was stirred for 15 seconds at a low speed. To this mixture was added, with blending, 0.16 g zinc, then 0.16 g zinc oxide powder (Zinc Corp. of America; Monaca, PA). After 15 seconds of blending, 6 g alum was added with blending, and the binder precipitated onto the pulp. A slurry of 10 52.8 g silica particles that had been previously bonded with approximately 2 to 5 weight percent, based on the weight of the silica particles, SuperLig™ 304 extractant dispersed in 300 mL water was then added and blending was continued for 30 seconds.

A solid sheet was prepared from the slurry as described in Example 1. The 15 wet sheet was pressed for 5 minutes at 448 kPa, then dried at 104°C for 60 minutes to give a dry sheet.

### Example 8

A circular disk having a diameter of about 90 mm was die cut from the 20 sheet prepared in Example 7. This disk was placed in a stainless steel pressure holder (Cole Parmer Instrument Co.; Niles, IL) fitted with inlet and outlet pipes and washed with 500 mL deionized water at a flow rate of 55 mL/min. Thereafter, the disk was charged with an aqueous solution of copper sulfate (60 ppm Cu<sup>+2</sup>) at a flow rate of 55 mL/min.

25 At regular intervals, samples of the effluent stream were taken and analyzed for Cu<sup>+2</sup>. The results are given below in Table 2.

Table 2: Extraction of Copper Ions

Time (min)	[Cu <sup>+2</sup> ] (ppm)
2	0.6
4	0.5
6	0.3
8	0.5
10	0.6
15	0.3
20	0.5
25	1.0
30	1.0
35	5.4
40	15.8
45	28.9
50	40.4
55	47.9
60	52.2

The data of Table 2 show that the first significant appearance of Cu<sup>+2</sup> in the effluent occurred after approximately 30 minutes and that the sheet was 5 saturated with Cu<sup>+2</sup> after about 60 minutes. This shows that the capacity of an SPE sheet of the present invention for metal ions in aqueous solutions can be considerable.

#### Example 9

10 Two 20.3 cm × 20.3 cm squares were cut from the sheet prepared in Example 7. One of these squares was soaked in water for one week while the other was kept in ambient air.

The square kept in air was subjected to treatment in a blade pleater (Robafsky GmbH; Berlin, Germany), but the square split into two pieces at the first pleat.

The water-soaked sheet was wrapped with a 40 × 24 strand aramid scrim (DuPont) which weighed approximately 220 g/m<sup>2</sup>. This composite structure was also subjected to treatment in a blade pleater, and it was successfully formed into a pleated structure.

Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be unduly limited to the illustrative embodiments set forth herein.

We claim:

1. A solid phase extraction sheet for removing one or more chemical species dissolved or entrained in a fluid comprising:

5       a) a porous polymeric pulp, said pulp comprising a plurality of fibers;

b) from about 3 to about 7 weight percent of a polymeric hydrocarbon binder; and

c) entrapped in said pulp, particles that exhibit at least one of reactive and sorptive properties toward said chemical species,

10      said particles being present in an amount such that the weight ratio of particles to binder is at least 13:1, said sheet having an average uncalendered thickness and said particles having an effective average diameter such that the ratio of sheet thickness to particle diameter is at least 125:1.

15      2. The solid phase extraction sheet of claim 1 wherein said particle to binder weight ratio is at least 14:1.

3. The solid phase extraction sheet of any of claims 1 and 2 wherein said particle to binder weight ratio is at least 15:1.

20      4. The solid phase extraction sheet of any of claims 1 to 3 wherein said binder is present in an amount of about 5 weight percent.

5. The solid phase extraction sheet of claim 1 wherein said polymeric pulp comprises at least one of aramid, polyethylene, and polypropylene fibers.

25      6. The solid phase extraction sheet of any of claims 1 to 5 wherein said particles are sorptive toward said chemical species.

7. The solid phase extraction sheet of any of claims 1 to 6 wherein said sorptive particles are (1) a derivatized or underivatized inorganic oxide, or (2) derivatized or underivatized poly(styrene divinylbenzene).

5 8. The solid phase extraction sheet of any of claims 1 to 7 wherein said sheet is dried.

9. The solid phase extraction sheet of any of claims 1 to 8 wherein said sheet is pleated.

10

10. A cartridge device comprising the pleated sheet of claim 9.

## INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/US 96/01628A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B01J20/28 B01D39/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,94 11556 (HOECHST CELANESE CORP.) 26 May 1994 see page 20-29; claims 1-15 ---	1,6,7
A	US,A,4 512 897 (CROWDER, III) 23 April 1985 see column 10, line 59-62 see column 33-36; claims 1-30 ---	1-8
A	EP,A,0 432 438 (KURARAY) 19 June 1991 see page 12; claims 1-9 ---	1,5
A	WO,A,93 06924 (MINNESOTA MINING AND MANUF.) 15 April 1993 see page 36-38; claims 1-12 ---	1-8
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 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
17 May 1996	28-05- 1996
Name and mailing address of the ISA European Patent Office, P.B. 5818 PatentUaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl. Fax (+ 31-70) 340-3016	Authorized officer  Wendling, J-P

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 96/01628

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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